Mathematical Modelling of Lithium-ion Concentration in Rechargeable Lithium Batteries

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Abstract

The demand for lithium ion batteries has increased due to the increasing need by consumers for rechargeable batteries. In the effort to produce high performance batteries, mathematical model becomes a vital instrument in helping batteries developers to understand the behaviour of the battery systems during charge and discharge process. This understanding is useful in the optimization of the battery design and parameters. This paper presents a mathematical model used to simulate the intercalation process of lithium ions in the electrode of a lithium-ion battery. This model is used to study the intercalation process through the lithium-ion concentration profiles during charge/discharge of a rechargeable lithium-ion battery. This approach resulted in solving the diffusion equation in the solution phase and the solid phase of the battery. Results from both phases are plotted and compared.

1. Introduction

Mathematical modeling of electrochemical systems that includes porous electrodes is based on governing equations for the dependent variables of interest. Originally, (Bird *et al* 1960) presented a thorough review of many equations similar to those needed for porous electrodes. However, Newman and his friends (Newman and Tiedemann 1975, Newman 1991) were among the first to associate these equations to the diffusion process in porous electrodes and electrochemical systems. In electrochemical systems, comprehensive models have been employed to study many batteries as lead-acid (Sunu 1984, Gu et al 1997), nickel-cadmium (Fan & White 1991, De Vidts & White 1995, Ratnakumar et al 1996), nickel-metal hydride (Paxton & Newman 1997, De Vidts et al 1995, Heikonen 1996) and lithium-ion (Fuller et al 1993 & 1994, Doyle & Newman 1995, Doyle et al 1996, Hashim Ali et al 2000, 2006 & 2008). In designing a battery model, a good model must be able to capture the species and charge transfer across the battery and the microscopic phenomena occurring inside the active material and the electrolyte/electrode interface. This is due to the fact that the rate of the electrochemical reactions in a battery is largely governed by these microscopic and interfacial phenomena.

Many authors (West *et. al*. 1982, Atlung *et. al*. 1984, Fuller *et. al.* 1993 &1994, Doyle & Newman 1995, Doyle *et. al*. 1996, Darling and Newman 1997 & 1998, Mao and White 1993, Nagarajan *et*. *al* 1998 and Botte *et. al.* 2000) have used either solid or solution diffusion process to model the intercalation/deintercalation of lithium ions in the electrode.

2. Battery Model

Figure 1 shows the schematic representation of a cell sandwich of a closely packed anode employing a solid lithium foil as negative electrode, a lithium transition metal oxide and $LiMn_2O_4$ active material in the positive electrode. The electrolyte is a liquid comprising lithium-hexaflourophosphate $LiPF_6$ in a mixture of equal volumes of ethylene carbonate (EC) and dimethyl-formamide (DMF). The lithium cell is divided into three regions: the negative electrode, separator and positive electrode. The negative electrode is a solid lithium foil. The positive electrode is an insertion-type porous electrode. During discharge, lithium-ions de-intercalate from the anode, diffuse through the separated and intercalate into the cathode.

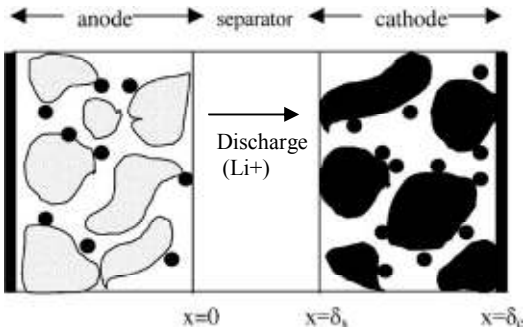

Figure 1 Schematic view of the $LiMn_2O_4$ full-cell

2.1 Solid Phase

In this phase, the mathematical model developed aimed to simulate the transport mechanism of lithium ions into the active materials in the porous electrode under solid diffusion limitations. This transport mechanism is modeled as a material balance equation using Fick's Law. The modeling is done by solving the diffusion equation in a particle of the electrode. An electrode with irregularly shaped pores and cavities is difficult if not impossible to describe mathematically. Hence, in developing a model for this solid phase diffusion limitation, the porous electrode is considered to have a specific geometry such as solid spheres. This geometry consist of equally sized particles uniformly distributed in the electrode and packed in such a way that all particles are in electronic contact with the current collector. This is to ensure that porosity does not change significantly in any directions within the electrode.

In this approach, the solid particle in the electrode is assumed to be a sphere of radius R as shown in Fig. 1. The transport of the species, written in spherical coordinates, is given by

$$\frac{\partial c_s}{\partial t} = D_s\left[\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r}\frac{\partial c_s}{\partial r}\right] \tag{1}$$

where the subscripts *s* denotes the solid sphere. The initial condition and boundary conditions are

$$c_s(r,0) = c_0\,,\ \frac{\partial c_s(0,t)}{\partial r} = 0 \text{ and } -D_s\frac{\partial c_s(R,t)}{\partial r} = j_n \tag{2}$$

where c_0 is the initial concentration of lithium ion in the solid particle, D_s is the diffusion coefficient inside solid electrode particle and $j_n = I/aFL_c$. Here, I is current density, a is specific interfacial area and F is Faraday's constant. The negative sign indicates that the pore wall flux j_n across the solid interface is in the opposite direction to the lithium ion diffusion into the surface of the insertion material.

2.2 Solution Phase

The governing equation for the electrolyte concentration in the solution phase is given as

$$\frac{\partial}{\partial t}c(x,t) = D\frac{\partial^2}{\partial x^2}c(x,t) + \frac{aj_n\left(1-t_+^0\right)}{\varepsilon} \tag{3}$$

where c (x, t) is the material balance of salt in the solution phase subject to boundary and initial conditions

$$\frac{\partial c(L_s+L_c,t)}{\partial x} = 0\,,\ \frac{\partial c(L_s,t)}{\partial x} = \frac{I\left(1-t_+^0\right)}{FDc_0\varepsilon^{3/2}} \text{ and } c(x,0) = c_0\,. \tag{4}$$

Here, D id the diffusion coefficient of the lithium-ion in the electrolyte, ε is the volume fraction of the solid, t_+ is the transference number, a is the specific interfacial area and j_n is the pore wall flux of lithium-ion.

In order to facilitate calculation, we introduced dimensionless parameters

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Using these dimensionless parameters, equation (1) is then linearized and solved using Laplace Transform.

3. Result and Discussions

In order to obtain the analytical solution to this diffusion problem, eqn. (1) is first linearized eqn. and then solved using Laplace transform. Upon inversion for n = 1 and k = 1, we get

$$c_s(\rho,\tau) = c_0 + \frac{Rj_n}{D_s\rho}\left[-\exp(-1+\rho+\tau)\,erfc\left(-\sqrt{\tau}+\frac{1-\rho}{2\sqrt{\tau}}\right)+erfc\left(\frac{1-\rho}{2\sqrt{\tau}}\right)+exp(-1-\rho+\tau)\,erfc\left(-\sqrt{\tau}+\frac{1+\rho}{2\sqrt{\tau}}\right)-erfc\left(\frac{1+\rho}{2\sqrt{\tau}}\right)\right] \quad (5)$$

where $\rho = r/R$ and $\tau = D_s t/R^2$ are two dimensionless variables. However, when tested for validity, this equation is valid only for short discharge time t. In order to obtain a solution for longer discharge time, it is necessary to rewrite the transformed equation in a hyperbolic form and used Maclaurin series and then inverse it as

$$c_s(r,t) = c_0 - \frac{j_n R^2}{D_s}\left\{\frac{3D_s t}{R^2}+\frac{1}{2}\left(\frac{r}{R}\right)^2-\frac{3}{10}-2\left(\frac{R}{r}\right)\sum_{n=1}^{\infty}\frac{\sin(r\alpha_n/R)}{\alpha_n^2\sin\alpha_n}\exp\left(-\alpha_n^2 D_s t/R^2\right)\right\} \quad (6)$$

where α_n's are the positive roots of $\alpha_n \cot \alpha_n = 1$. Equation (3) is valid for all t.

Eqn. (3) is converted to dimensionless parameters and solved using Laplace transformation to get

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where $\beta = (m\pi)/r$. This equation is valid for all discharge time and is related to the charge/discharge coefficient. Since current lithium batteries have discharge time more than 2 hours, we have omitted the short-time solution in this paper.

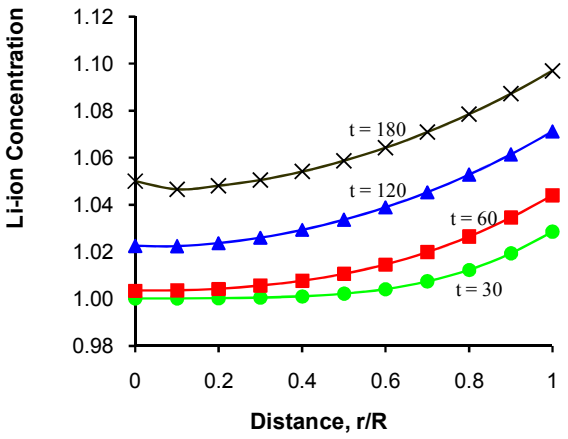

Figure 2 Lithium ion concentration in solid phase for short time (t = 30, 60, 120 and 180 sec)

Equations (5) and (6) are plotted against dimensionless distance in Figure 2 and 3, respectively. Fig. 2 depicts the graphs of concentration versus distance in the cathode for short time interval in the solid sphere case at a constant discharge current of 1.39 mA/cm^2. These plots exhibit a hyperbolical increase in concentration as the lithium ions move from the centre to the surface of the electrode particle.

Fig. 3 gives the concentration profiles inside solid sphere particle for large time interval at a constant discharge current of 1.39 mA/cm^2. Similar to figure 2, the graphs suggested that during discharge lithium ions inside a solid particle move away from the centre of the spherical particle. This is due to the fact that lithium ions are moving towards the surface of the particle in order to be dispersed into the electrolyte in the cathode region. The lithium ions concentration increases in a consistent rate and becomes more rapid as time gets larger. For a very small time interval, the climb in lithium ion concentration is rather slow as shown in fig. 2 as compared to the increase during a longer time interval in fig. 3. This is due to the fact that very small amount of lithium ions have been dispersed in this short period.

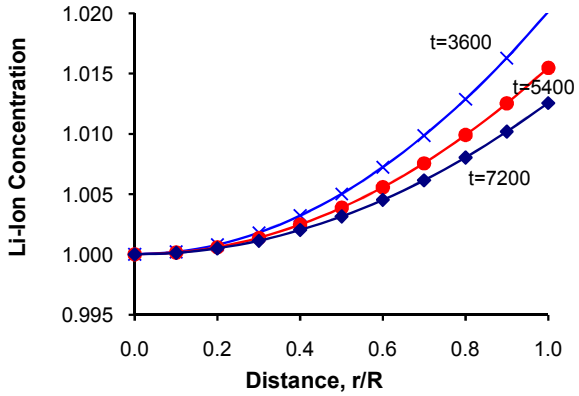

Figure 3 Lithium–ion concentration in solid phase for long time (t = 3660, 5400, and 7200 sec)

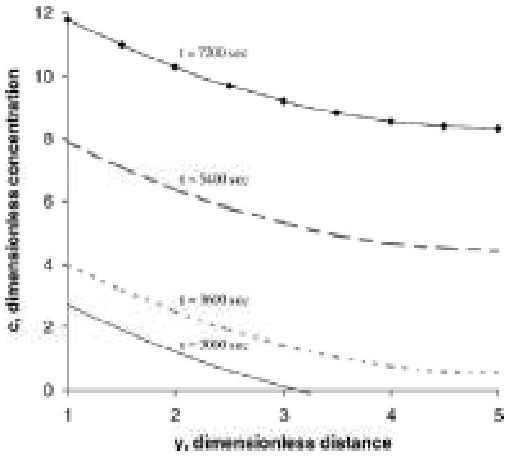

Figure 4 Lithium–ion concentration in solution phase during discharge of I = 1.39 mA/cm^2

Fig. 4 and 5 are plotted using eqn. 7 where the solid volume fraction ε is taken to be 0.524 (Doyle & Newman, 1997) and the initial concentration is 3.9 mol cm^{-2}. Figure 4 shows the filing up of the cathode for a constant discharge current at various times. It is observed that the concentration of lithium ions is the lowest at the back of the cathode. At the beginning of discharge (t = 3000 sec), the discharge current sends the lithium ions until y = 3.12 into the bulk of the cathode. As time increases, more lithium ions enter the cathode and reach the back at the cathode. Fig. 5 shows the graph of discharge curves at fixed time for various discharge currents. Again the concentration is minimum at the back of cathode. This is due to the fact that during discharge, lithium ions fill up the back portion

of the cathode last. During full charge, the lithium ion concentration is cathode is almost zero and so it is expected that during discharge, the back portion of cathode will be fill up last.

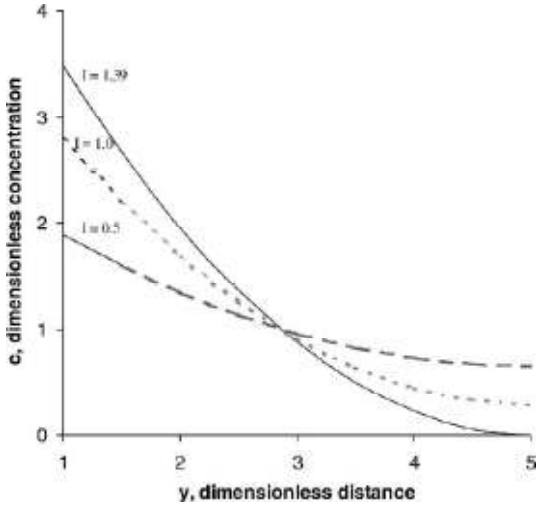

Figure 5 Lithium–ion concentration in solution during discharge of I = 0.5, 1.0 and 1.39 mA/cm^2

4. Conclusion

In this work, the intercalation and deintercalation of lithium ions in the cathode has been modeled as a diffusion process by solving the material balance equation in the electrode of a battery. This model is assumed to be isothermal with a constant diffusion coefficient. Two cases have been considered. In the first case, we considered diffusion in a spherical shape particle in a solid phase; while in the second case, the diffusion occurred in the solution or the electrolyte phase. Results from both cases are presented. The graphs obtained agreed with the intercalation theory of the lithium ions inside a cell and showed good agreement with the results reported by Fuller *et al*. [16, 17].

Even though there has been a lot of work on mathematical modeling of lithium ion batteries, most of the work was done numerically [15-17, 26-30]. Very few analytical works are available in the literature. To the author's knowledge, Atlung *et. al*. [24-25] were among the first to publish their analytical work on rate limitations in the composite insertion electrode. They solved Fick's Law to study the dynamic aspects of solid solution cathode for battery system based on lithium metal anode and TiS_2 intercalation compound cathode and obtained solutions for solid phase diffusion limitation. However, their work only gives solutions for lithium-ion diffusion with constant flux density on the surface of the cathode particle by making an assumption that the initial lithium ion concentration is zero. This contradict the fact that there is a certain amount of lithium ion exist in the electrolyte and cathode material of the cell. Hence, this present work considers a constant lithium ion concentration in the initial condition.

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